The Effects of Crowding in Dendronized Polymers

Paul M. Welch, T-14, and Cynthia F. Welch, LANSCE-12

Many exponents of nanotechnology tout supramolecular assemblies as potential structural and functional building blocks in a host of devices. The envisioned constructions require materials with several physical characteristics, including a well-defined shape, tunable dimensions, slow relaxation dynamics, the possibility of possessing a large number of chemically active sites, a propensity for self-assembly, and stimuli-responsive local conformations. Dendronized polymers, linear chains with grafted dendrons as schematically pictured in Fig. 1, have recently garnered much attention in the synthetic chemistry literature because they offer many of these traits. Experimental studies indicate that for low degrees of polymerization, the polymer adopts a spherical conformation. However, as the chain's contour length increases, the steric crowding of the side-chain dendrons forces the polymer backbone into an extended or possibly helical conformation, giving the molecule an overall cylindrical or rod-like shape. The length and radial extent of these polymers may be controlled by the number of repeats along the backbone and the generation of growth of the attached dendrons. As recently demonstrated by Das and coworkers, these assemblies behave like single-molecule glasses with relaxation dynamics characterized by stretched exponentials; thus, once assembled into a device, they may be expected to stay in place rather than hopping about as would be expected for more common synthetic polymers. Because their girth derives from the basic building blocks of dendrimers, dendronized polymers may offer many of the same benefits as dendrimers, including a large number of functional moieties at the dendron termini and a tunable density profile. Applications envisioned for these molecules include roles in nanoelectronics, catalysis, biotechnology, and molecular device fabrication.

The large size and often-poor solubility of dendronized polymers makes their characterization challenging, however, and many basic questions regarding their conformational statistics stand open. Though some single-chain studies have been performed, our understanding of the effect that the topological parameters have on the physical properties of these materials remains incomplete. We lack a clear picture of how properties such as the size-mass scaling, the cross-sectional size, the terminal group accessibility, the extent of dendron interpenetration, and the polymer conformation are affected by dendron generation *(G)*, degree of polymerization *(DP)* and the spacing between dendrons along the backbone *(S)*. A better understanding of these trends will improve our ability to tune the polymer's physical properties through chemical design. Thus motivated, we report here the results from computer simulations performed to investigate in a controlled manner the effects of *G, DP,* and *S* on both the local and global conformation of locally flexible dendronized polymers. Our results verify some speculation and conjecture found in the literature as well as offer new insight into the importance of steric crowding in these materials. Significantly, we find that the dendrons become extended away from the main chain backbone as *S* decreases, accompanied by a compression of the dendrons and a higher occupancy of the terminal groups near the surface of the molecule.

Dendrimers do not interpenetrate, thus their Newtonian rheological behavior. This exclusiveness should carry

over to the dendronized polymers and is speculated to be the central conformational feature responsible for many of their physical properties. This trait also holds significance for device fabrication; if the dendrons do not interpenetrate, then each dendronized polymer can be viewed as an independent building block. Figure 1B contains an image of a typical conformation from the simulations of a $DP = 100$, $G = 5$, $S = 2$ molecule. All of the dendrons are identical, but are colored to more easily illustrate dendron segregation. Indeed, the dendrons do not appear to interpenetrate. As shown below, the generation G and spacing S of the dendrons dictate the dimensions and physical layout of these molecules as a result of this segregation.

This segregation results in the relegation of the dendrons further away from the chain backbone and affects the accessibility of any chemical functionality present. Plotting the spherical distribution of terminal groups of a dendron about its attachment point along the backbone, $\rho(r)$, for $G = 5$ and $DP \approx 50$ for a range of S values illustrates this, as shown in Fig. 2. For large values of S, the terminal groups distribute themselves in a roughly Gaussian fashion in the effective tube. However, as S decreases and steric crowding begins to force the dendrons further away from the tube axis, the distribution of terminal groups changes dramatically; they segregate preferentially toward the tube surface. This surface segregation of the terminal groups has been proposed to exist in dendrimers, though most experimental and theoretical studies seem to negate this possibility without the introduction of dendron stiffness. Here, however, we observe this sought-after trait in fully flexible molecules. Moreover, while the molecular weight, and thus the number of terminal groups, that can be synthetically achieved in their dendritic precursors is limited, dendronized

polymers can continue to add terminal groups by merely increasing DP while holding S constant.

We will report further details on the properties of these curious molecules in a future publication, including evidence for the linear growth of the "tube" diameter with G, the compression of the dendrons, and the glob-to-coil transition. This work was supported under LDRD / ER Computational Schemes for Multiscale Modeling of Polymers, T. D. Sewell, P. I.

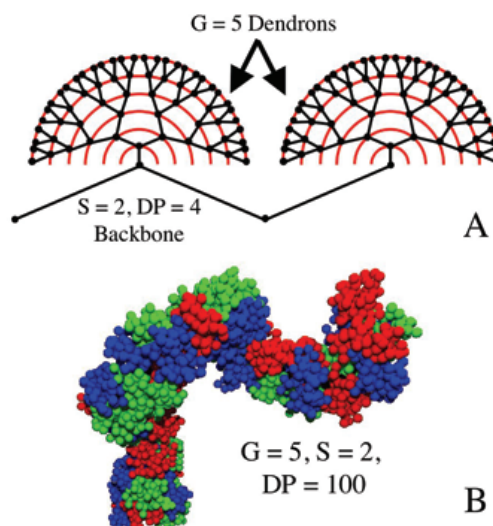*For more information contact Paul Welch at pwelch@lanl.gov.*

Fig. 1.
A) The topology studied and nomenclature applied here, as exemplified by a $G = 5$, $S = 2$, $DP = 4$ dendronized polymer. B) A representative configuration observed in simulations of $G = 5$, $S = 2$, $DP = 100$ dendronized polymers. Dendrons are colored to highlight segregation.
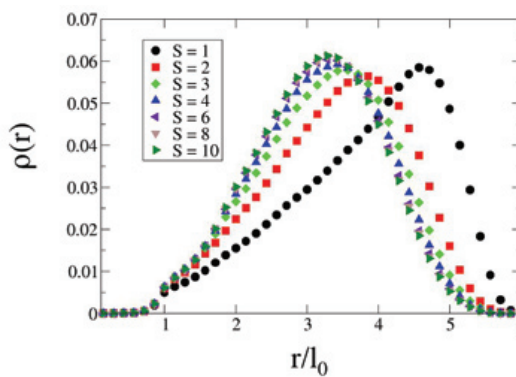

Fig. 2.
The radial density $\rho(r)$ of terminal groups about their respective attachment points along the main chain backbone versus the radial distance r normalized by the equilibrium bond length l0.